PREPARATION, CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/MUSCOVITE NANOCOMPOSITE

by

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DECLARATION

I declare that this thesis is the result of my own research, that is does not incorporate without acknowledgement any material submitted for a degree or diploma in any university and does not contain any materials previously published, written or produced by another person except where due reference is made in the text.

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LIST OF ABBREVIATIONS

3D	Three dimensional
2D	Two dimensional
1D	One dimensional
PLSN	Polymer layered silicate nanocomposites
MMT	Montmorillonite
PP	Polypropylene
PP/M	Polypropylene/Muscovite
PP/OM	Polypropylene/Organomuscovite
PE	Polyethylene
PA	Polyamide
PS	Polystyrene
CTAB	Cetytrimethylammonium bromide
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
TEM	Transmission electronic microscopy
SEM	Scanning electron microscopy
DSC	Differential scanning calorimeter
TGA	Thermo gravimetric analysis
CEC	Cation exchange capacity
PP-g-MAH	Polypropylene-grafted maleic anhydride
PP-POSS	Polypropylene-methyl polyhedral oligomeric silsesquioxane

TPO	Thermoplastic olefin
GM	General Motors
ASTM	American society for testing and materials
FESEM	Field emission scanning electron microscopy
M	Muscovite
OM	Organomuscovite
DTG	Derivative thermogravimetry
OMMT	Organmontmorillonite

LIST OF SYMBOLS

wt%	Weight *percent*
TPa	Terapascal
meq	milliequivalents
g	Gram
nm	Nanometer
%	Percent
^{0}C	Degree celsius
min	Minute
cm	Centimeter
μm	Micrometer
MPa	Megapascal
^{0}	Degree
ΔH_m	Melting enthalpy of composite specimen
ΔH^0_m	Melting enthalpy of 100% crystalline polymer
J/m	Joule per meter
T_m	Melting temperature
T_c	Crystallization temperature
X_c	Degree of crystallinity
T_{max}	Maximum decomposition temperature

PENYEDIAAN, PENCIRIAN DAN SIFAT-SIFAT NANOKOMPOSIT POLIPROPILENA/MUSKOVIT

ABSTRAK

Dalam kajian ini, nanokomposit polimer berlapis silikat yang mengandungi polipropilena (PP) dan muskovit telah disediakan menggunakan kaedah penyebatian leburan. Polipropilena tercantum maleik anhidrida (PP-g-MAH) dan polipropilena metil polihedral oligomerik silsesquioxane (PP-POSS) telah digunakan untuk menserasikan sistem komposit PP/Muskovit. Pada mulanya, tanah liat muscovit dirawat dengan nitrat litium ($LiNO_3$) dan diikuti dengan cetiltrimethilammonium bromida (CTAB) melalui rawatan pertukaran ion untuk memperolehi organomuskovit (OM). Kehadiran alkil ammonium di dalam OM telah dicirikan dengan menggunakan Perubahan Infra Merah (FTIR). Corak pembelauan sinar-X (XRD) OM menunjukan bahawa ruang jarak antara lapisan dalam muskovit telah meningkat daripada 0.99nm kepada 1.22nm. Kekukuhan dan kekuatan nanokomposit PP/muskovit telah meningkat dengan kehadiran OM dan penserasi. Keputusan daripada pembelauan sinar-X (XRD) dan mikroskop elektron transmisi (TEM) mendedahkan pembentukan struktur interkelasi. Melalui pemeriksaan menggunakan mikroskop imbasan electron pancaran medan (FESEM) menunjukkan bahawa penggunaan OM mempamerkan penyebaran pengisi yang lebih baik dan ianya lebih ketara dengan penambahan penserasi. Di samping itu, keputusan analisa terma mendedahkan bahawa suhu lebur (T_m) dan tahap hablur (X_c) nanokomposit telah menurun tetapi suhu penghabluran (T_c) telah meningkat dengan penggunaan OM. Analisis termogravimetri (TGA) juga mengesahkan bahawa kestabilan terma telah bertambah baik dengan penambahan OM dan penserasi.

PREPARATION, CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/MUSCOVITE NANOCOMPOSITE

ABSTRACT

In this study, polymer layered silicate nanocomposites containing polypropylene (PP), compatibilizer and organomuscovite were prepared by melt compounding. Polypropylene grafted maleic anhydride (PP-g-MAH) and polypropylene methyl polyhedral oligomeric silsesquioxane (PP-POSS) were used to compatibilize PP/muscovite systems. Muscovite clay particles were initially treated with lithium nitrate ($LiNO_3$) and followed by cetyltrimethylammonium bromide (CTAB) through ion exchange treatment to obtained organomuscovite (OM). The presence of the alkyl ammonium ions in the OM were characterized using Fourier transform infrared (FTIR) analysis spectroscopy. X-ray Diffraction (XRD) diffractograms of OM shows that the basal spacing of muscovite was expanded from 0.99nm for the OM to 1.22nm. The stiffness and strength of PP/muscovite nanocomposites were increased with the presence of OM and compatibilizer. X-ray Diffraction (XRD) and Transmission electron microscopy (TEM) results revealed the formation of intercalated structure. Field Emission Scanning Electron Microscopy (FESEM) examination showed that the present of OM exhibit better dispersion and become more significant with the addition of compatibilizer. Furthermore, thermal analysis results revealed that melting temperature (T_m) and degree of crystallinity (X_c) of nanocomposite were reduced but the crystallization temperature (T_c) were increased with the used of OM. TGA also confirms

that the thermal stability of the nanocomposites were improved with the addition of OM and compatibilizer.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Polymer nanocomposites have become one of the most popular areas of current research and development due to the remarkable properties exhibited by these materials. It is a combination of two phase materials in which one of the phases is dispersed in the matrix on a nanometer scale. Traditionally, macrometer fillers were used as filler in order to enhance the properties of the polymer composites as well as to reduce cost. However, the used of these types of fillers brought some drawbacks, such as high in weight, brittleness and loss of transparency of the composites. This is because it requires a large amount of filler to incorporate to the polymer materials. Based on this problem, a lot of research have been carried out and polymer nanocomposites were produced as the solution. The reason behind the remarkable properties that polymer nanocomposites offer are mainly due to the small interparticle distances and the conversion of a large fraction of the polymer matrix near their surfaces into an interphase of different properties (Brechet et al., 2001).

The nanocomposites can be classified into three categories in which can be distinguished based on the virtue of the primary filler particle dimensions that fall in nanometer range. Three dimensional (3D) filler is in the form of spherical like silica particle, carbon nanotube is classified as two dimensional (2D) and plate-like nanofiller such as monmorillonite clay is one dimensional (1D). Among the entire nanocomposite, those based clay (polymer layered silicate) are the most widely investigated due to its

availability and low cost. Polymer layered silicate nanocomposites (PLSN) is a new class of composite materials composed of hybrid organic polymer - inorganic materials (Giannelis, 1996; Ogawa and Kuroda, 1997; Okada and Usuki, 1995). Over the past decade, PLSN is increasingly popular due to the enhancement in terms of engineering properties such as strength and modulus under tensile and flexural loading conditions (Li et al., 2007; Giannelis, 1998; Fornes et al., 2002; Giannelis, 1996), thermal stability (Zhang and Wilkie, 2006; Lebaron et al., 1999; Alexandre and Dubois, 2000), gas impermeability (Gilman et al., 1999; Ahmadi et al., 2004) and flammability (Gilman et al., 1997; Gilman et al., 1998) that are achievable at low filler loading, typically less than 5 wt%. The key to this improvement is the ability of the layered silicate to exfoliate, dispersed individually and high aspect ratio silicate platelets within the polymer matrix.

Layered silicates are clay minerals, built of two structural units. The simplest is the 1:1 structures (example: kaolinite) where a silica tetrahedral sheet is fused to an aluminium octahedron and sharing the oxygen atoms and the other one is 2:1 structures which are commonly used in PLSN. Montmorillonite (MMT) (Mittal, 2007; Mandalia and Bergaya, 2006; Jimenez et al., 1997) and saponite (Alexandre and Dubois, 2000; Bharadwaj, 2001; Kojima et al., 1993b) are classified in the 2:1 structure and among the most commonly used layered silicates in producing PLSN due to their ion-exchange properties and swelling behaviour. However, to render layered silicate with polymer matrices, there are two major problems that need to be considered. First, the layered silicate is not easily dispersed in polymers due to their preferred face to face stacking in agglomerated tactoids and second, the tactoids cannot be dispersed into the discrete

monolayers due to the intrinsic incompatibility of hydrophilic layered silicates with hydrophobic polymer (Pavlidou and Papaspyrides, 2008). In order to overcome this problem, the hydrophilic silicate surface needs to be modified to an organophilic to make it compatible to the organic polymer matrices in achieving their exfoliation. Generally, this modification can be done by ion exchange treatment with cationic surfactant including primary, secondary, tertiary and quaternary alkyl ammonium or alkylphosphonium. Commonly used alkyl ammonium modifications include octadecyltrimethyl ammonium, dioctadecyldimethyl ammonium and dimethyldioctadecyl ammonium (Osman and Rupp, 2005; Mittal, 2007). It is used to lower the surface energy of the silicate surface and increase the wettability of the filler particle with the polymer matrix. Thus gives better interaction between two phases.

Polymer layered silicate nanocomposites have been synthesise from a variety of layered silicates and polymers such as polypropylene (PP), polyethylene (PE), nylon and epoxy. Toyota Central Research and Development Labs the pioneer in developing a polymer layered silicate nanocomposite based on nylon 6 matrix in 1988 (Subramaniyan and Sun, 2006). After that, many researchs have been done regarding on polymer layered silicate nanocomposite (Ahmadi et al., 2004; Aldousiri et al., 2011; Bhattacharya et al., 2008). PE and PP are among the most widely used commodity thermoplastics in the synthesis of polymer layered silicate nanocomposites due their availability and low cost. However, the expected properties could not be achieved due to their hydrophobic nature and lack of favorable interaction with the layered silicate. Thus, phase separated system occurred. So, modification on the layered silicate and the use of suitable

functional compatibilizer were needed to synthesis polypropylene layered silicate nanocomposite.

1.2 Problem statement

As what had been mentioned earlier, monmorillonite (MMT) is one of the most widely used layered silicate in synthesis PLSN. However, there are also other types of clays, has attracted much less attention which are equally potential such as vermiculite and muscovite. These clays are belong to 2:1 layered structure and have a different of layer charge density, layer charge site, and charge distribution. Muscovite, in specific has the highest layer charge density. In addition, it has high aspect ratio and much cheaper than MMT. The general formula of Muscovite is $KAl_2(AlSi_3)O_{10}(OH)_2$. It is composed of monoclinic structure with a very high layer charge density, close to 1.0 equivalent per $O_{10}(OH)_2$. Although muscovite belong to 2:1 layered structure which is known as swelling clay but it has a few differences as compared to others. First, it has a very high layer charge density and second, it has homogenous charge distribution in which comes from the outside tetrahedral sheet of the aluminosilicate layer (Yu et al., 2006). Thus, it does not swell in water and not easily intercalate. Furthermore, the studies on using muscovite as filler have not yet been explored extensively and it is locally available in Malaysia. Its have been report that the annual production of muscovite has stayed around 3,700 tonnes and most of Malaysia's muscovite production are exported to Japan, Thailand, North Korea, Taiwan and South Korea (Tse, 2007). The aim of this study is to synthesis PLSN composed of polypropylene as the matrix and muscovite as the filler. Two stages of ion exchange treatment will be carried

out, in order to produce polypropylene/muscovite nanocomposite and hence enhance the mechanical and thermal properties of the nanocomposite.

1.3 Objective of the research

The main objectives of the research are:

1. To produce ion exchange treated muscovite particle for composite reinforcement filler.
2. To optimimize the ion exchanges treatment parameters based on concentration of $LiNO_3$ and CTAB for producing organomuscovite (OM).
3. To study the optimum muscovite loading for intercalated and exfoliated polypropylene/muscovite nanocomposite.
4. To study the effect of compatibilizer and cation exchange capacity (CEC) ratio on polypropylene/muscovite nanocomposite.

1.4 Scope of the research

This research proposed to fabricate, characterize, and investigate the properties of polypropylene/muscovite nanocomposites for engineering application**.** Melt compounding method is chosen due to the main advantage which is more economical as compared to others and it is compatible with current industrial mixing and processing techniques. Furthermore, this research will utilise the locally available muscovite which is much cheaper than monmorillonite in attempt to reduce the cost of layered silicate nanocomposites and hence become more competitive than conventional composite. Ion

exchange treatment will be done with two stages. In the first stage, it is treated with lithium nitrate and then with cetytrimethylammonium bromide (CTAB) to produce organomuscovite and obtain homogenous dispersion within the polymer system. The effect of ion exchange treatment to the mechanical and thermal properties of nanocomposite will be investigated. An X-Ray Diffraction (XRD) technique is used to identify intercalated structures by measuring the interlayer spacing of the silicates. The FTIR analysis will be used to analyze the effectiveness of ion exchange treatment on the muscovite particle. Meanwhile, the nanostructure of nanocomposites and the dispersion of muscovite will be attempt by Transmission electronic microscopy (TEM) and the distribution of layered silicates is evaluated through SEM image of the sample after tensile test. The tensile, flexural and izod impact test will be performed to characterize the mechanical properties of the nanocomposite in term of strength and modulus. Furthermore, differential scanning calorimeter (DSC) and thermo gravimetric analysis (TGA) will be used to analyze the thermal properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction.

Polymer composites are materials consist of two or more components and two or more phases, which are mixtures of polymers with inorganic or organic additives having certain geometries such as fibers, flakes, spheres and particulates. The additives may be continuous (long fibers or ribbons) and discontinuous (short) as for example, short fibers, platelets and spheres or irregulars. Additives for polymer composites have been variously classified as reinforcements, fillers or reinforcing fillers.

Basically, fillers, being much stiffer and stronger than the polymer, usually increase its modulus and strength. Thus, it enhances the properties of the polymer and at the same time lowering the cost of materials by replacing the more expensive polymer. There are many kinds of fillers and additives available but of particular interest are the fillers that contribute to improve polymer properties, which are carbon nanotubes, nanofibres and clays. Among all the potential fillers, clays, especially layered clay minerals have attracted great interest in the past two decades as it is possible to achieve impressive enhancements of properties due to it characteristic (Ray and Okamoto, 2003). This enhancement occurred by utilizing specially designed organophilic clays as nanofillers in polymer composites (Usuki et al., 2005; Zeng et al., 2005). It is known as polymer layered silicate nanocomposites (PLSNs) (Lebaron et al., 1999). PLSNs have superior thermal, mechanical electrical, barrier, and optical properties (Gao, 2004; Ray and Okamoto, 2003).

2.2 Polymer Layered Silicate Nanocomposite

2.2.1 Introduction

Over the past decades, polymers were reinforced with synthetic or natural inorganic compounds in order to enhance their properties and reduced cost. These conventional fillers have given a significant enhancement in the composite properties but they require a large amount of fillers in the polymer system, which results in an increase in weight, brittleness, opacity as well as in the bulkiness of the composite materials (Alexandre and Dubois, 2000; Fischer, 2003a; Lagaly, 1999; Giannelis, 1996; Varlot et al., 2001; Fischer, 2003b). Based on the dimension of phases involved, it is classified as microcomposites. On the other hand, nanocomposite is a new class of hybrid materials in composite category, in which at least one dimension or component of the dispersed particles is in the nanometer range. These new kind of materials offer a possibility to explore new behaviours and functionalities superior to those of conventional materials and provide stiffness, strength, and reliability comparable to or better than the conventional polymer. The excellent properties that are exhibited by nanocomposites are derived from the organic and inorganic components.

Besides that, the enhancement properties of nanocomposite are obviously due to the effects of nanoscale fillers within the polymer system (Fischer, 2003b). Nanoparticles can influence the properties of the composites at very low volume fraction due to a small interparticle distances and the conversion of a large fraction of the polymer matrix near their surfaces into an interphase of different properties (Lagaly, 1999).

As a result, desired properties of the nanocomposites are usually achieved at low filler volume fraction; at the same time retain the macroscopic homogeneity and low density of the polymer. Besides that, the geometrical shape of the particles also is one of the important factors in determining the properties of the composites. The nanocomposites can be classified into three different categories, depending on the dimensions of the filler which are:

1. Three dimensions are in nanometer scale and in the form of spherical particles. Silica and carbon black are the most commonly used filler which are included in this class of materials (Varlot et al., 2001; Sinha Ray and Okamoto, 2003). They have been used over the past decade in specific application and available in many sizes from 500 to 10nm.
2. Two dimensions in nanometers scale and the third one is in the range of micrometers. Carbon nanotubes (see Figure 2.1) and whiskers are the examples of fillers included in this class. This types of filler especially carbon nanotube have become one of the commonly studied over the past 5 years due to their mechanical and electrical properties. Previous studies had reported that carbon nanotubes have young's modulus in the range of 1TPa but flexible (Ajayan et al., 2000).The extremely high stiffness would make these materials ideal reinforcements for composites.
3. Two dimensions in micrometers scale and the third one in nanometer scale, which is layered silicate. Nanofiller with only one dimension in the nanometer range can be achieved by platelets. Montmorillonite is the most commonly used as filler in this category (Kojima *et al.*, 1993b).

Among all the potential nanocomposite precursors, layered silicate based nanocomposites have been most widely investigated due to it availability and their intercalation chemistry has been studied for a long time (Sinha Ray and Okamoto, 2003).

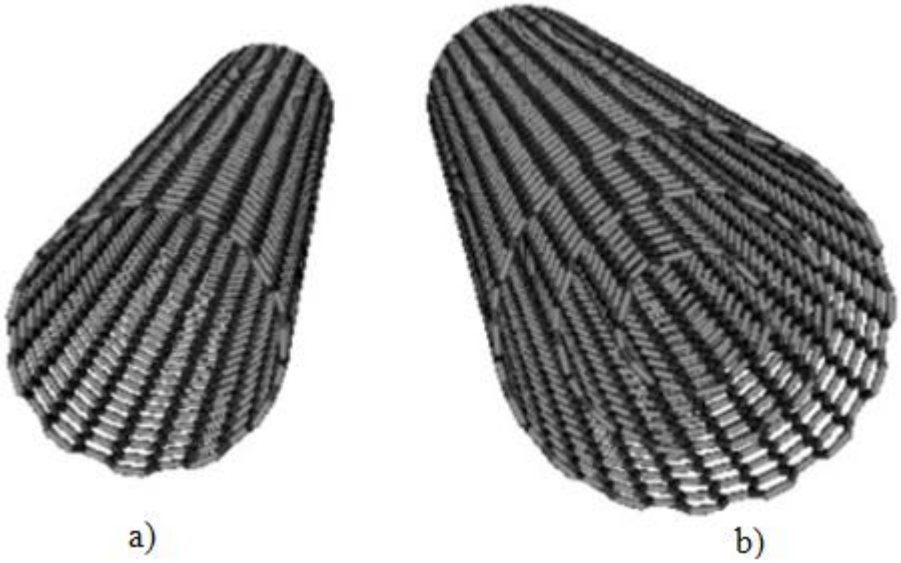

Figure 2.1: Structure of a carbon nanotube a) single-walled carbon nanotube (SWNT) b) multi-walled carbon nanotube (MWNT) (Tasis et al., 2006).

2.2.2 Layered silicate

Layered silicates have been widely used as reinforcement materials or filler in the polymer nanocomposite due to their abundance, high strength, larges interfaces and achieving considerable reinforcement at very small filler loading. Generally, layered silicates used in the synthesis of nanocomposites are natural or synthetic minerals, consisting of very thin layers that are usually bound together with counter-ions. The basic structure of layered silicate are tetrahedral sheets, where silicon is surrounded by

four oxygen atoms and octahedral sheets like aluminium is surrounded by eight oxygen atoms. As compared to conventional filler, it exhibits very high aspects ratios and very thin layer thickness which is around 1nm. Stacking of the layers leads to regular van der Waal gap between layer so called gallery or interlayer. Layered silicate has become most widely investigated as a filler in the synthesis of nanocomposites due to the ability of silicate particles to dispersed into individual layers and ability to fine-tune their surface chemistry through organic or inorganic modification (Giannelis, 1996). Compared to conventional composite only a low filler volume fraction is needed that can dispersed well into polymer system and create larger surface area for polymer filler interactions.

Three different types of polymer layered silicate nancomposite can be achieved depending on the strength of interfacial interaction between polymer matrix and layered silicate (see Figure 2.2):

(a) Phase separated composite :

polymer matrix has no interaction with layered silicate.

(b) Intercalated nanocomposites:

Insertion of polymer chains into the silicate structure occurs in a crystallographically regular fashion, regardless of the polymer to layered silicate ratio, and a repeat distance of few nanometers.

(c) Exfoliated nanocomposites:

Individual silicate layers are separated in the polymer matrix by average distances that totally depend on the layered silicate loading.

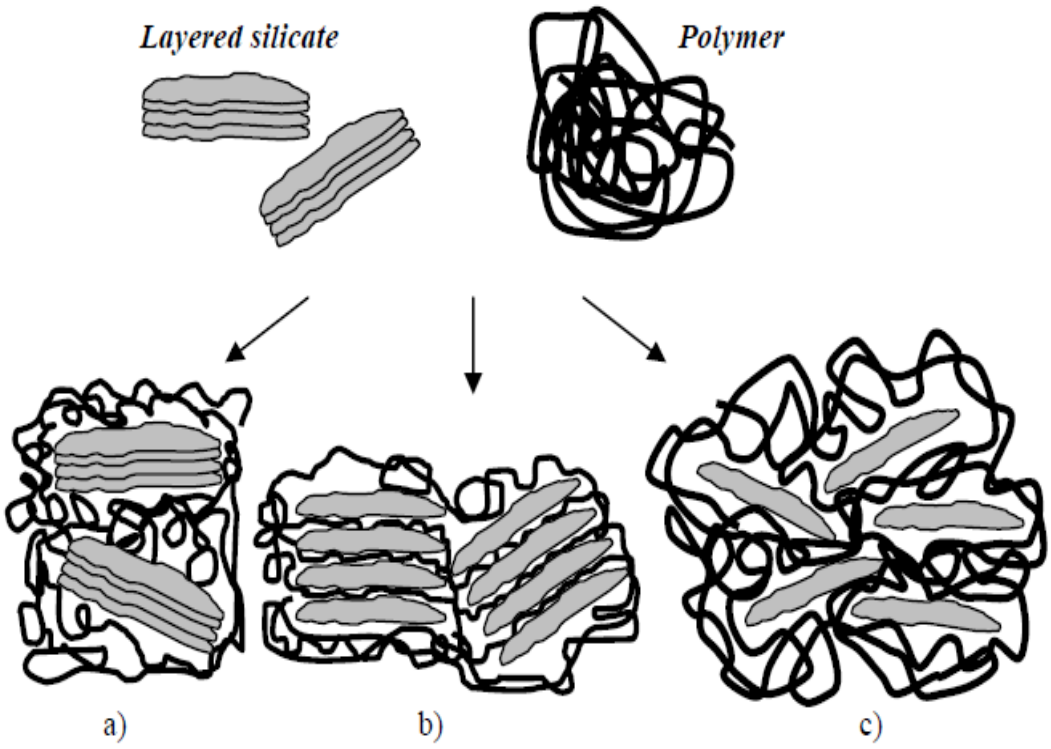

Figure 2.2: Schematic representation of the different types of composites generated based on the interactions of the layered silicate with polymer matrices. (a) Phase separated microcomposite, (b) intercalated nanocomposite and (c) exfoliated nanocomposite (Ray, 2006b).

The interest of using layered silicate in the preparation on nanocomposite has increased and many researchers started researching in this area due to the availability, low cost and enhancement that are offered by this material. Nevertheless, in order to produce PLSN, there is a problem of incompatibility between the filler and polymer matrix that needs to be solved because of the nature of layered silicate. As mentioned in the clay structure earlier in this chapter, modification is needed in order to obtain

organically modified silicates or clay and make it more compatible with the organic polymer matrices.

Generally, clay modification is needed in order to increase the interlayer spacing and improve clay-polymer compatibility by intercalate organophilic substance into the interlayer space of the layered silicate and weaken the interlayer interactions. Consequently, allowing macromolecules to penetrate into the interlayer space during process and forming uniform dispersion of clay layers in polymer matrix by the separation of individual layers. The use of organoclays in the formation of polymer layered silicate nanocomposites and their potential in improving a wide range of properties of polymers show multifunctionality of clay minerals in polymer composites (Nigmatullin et al., 2008).

Futhermore, Kojima et al (1993) said that, by using surfactant like alkylammonium as the replacement of the inorganic exchange cations in the cavities or "galery space" of the native clay silicate structure can compatibilize the surface chemistry of the clay and a hydrophobic polymer matrix. The stiffness, strength and dimensional stability in two dimensional exhibit by the PLSN are derived from the formation of layer orientation of the nanocomposite. In addition, because of the length of the scale involved that minimizes scattering, nanocomposites are usually transparent.

Beside that, PLSN also exhibits a significant increase in terms of thermal stability and self - extinguish characteristics. Since lower volume fraction of reinforcement were needed in order to get desired properties as compared to conventional composite, it significantly reduces the production cost and avoid inconvenient methods. Some commonly fabrication methods can be used such as extrusion and injection molding. Moreover, they are adaptable to films, fibers as well

as monoliths. The improvement of PLSN properties by incorporation of layered silicate is not a new subject, it had been studied long years ago (Theng, 1979; Blumstein, 1965). Two major findings have led to a renaissance of these materials. It had been reported that the first finding was on the research of polyamide (PA)-based nanocomposite containing synthetic and natural clays, containing very small amount of reinforcement loadings, at Unitika and Toyota research centers (Yasue et al., 1995; Kojima et al., 1993b; Kojima et al., 1993a). The second one was the series of observation by Vaia based on the possibility to melt-mix polymers with layered silicates, without the use of organic solvents (Vaia et al., 1993).

2.2.3 Types of Layered Silicate

There are two major classes of layered silicate, namely non-swelling and the swelling. The non-swelling, also known as the 1:1 family, are not swellable due to the forces that hold two adjacent clay layers (platelets) in place are colossal that the layers cannot move away from each other to accommodate any foreign species between them and the most common examples would be kaolinite and serpentine. The swelling, also known as the 2:1 family, have the ability to expand by incorporating foreign species in between adjacent clay tactoids. Saponite, montmorillonite and muscovite are the examples of swelling clays (Yu et al., 2006).

2.2.3.1 Montmorillonite

Montmorillonite is one of the most common types of layered silicates used as fillers in polymer nanocomposites due to is environmentally friendly, availability and its intercalation chemistry is well understood. The chemical formula of MMT is

$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ (M represents exchangeable cation and x is the layer charge).Generally, MMT exhibit cation exchange capacity (CEC) in the range of 90-110 meq/100 g and particle length of 100-150 nm (Ray, 2006a). It is expandable-layered silicate and can be intercalated / exfoliated into nanocomposites. MMT consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers(Paul and Robeson, 2008). The galleries of this clay can be expanded due to the hydration of the sodium ions and make the clay swell. This sodium ion can be exchanged with organic cations such as ammonium salts and form organoclay.

2.2.3.2 Muscovite

Muscovite is a clay mineral of special interest because of its well-defined crystal structure, molecularly smooth surface, and outstanding corona resistance (Brindley et al., 1980). Muscovite belongs to monoclinic structure with the space group (C2/c), with the cell parameter a = 5.18 Å, b = 8.99 Å, c = 20.07Å, β = 95.751^o (Liang and Hawthorne, 1996). These clays belong to 2:1 layered structure, which is the same crystal structure as MMT but has a different of layer charge density, layer charge site, and charge distribution. Muscovite, in specific has the highest layer charge density and homogeneous charge distribution. In addition, it has high aspect ratio than MMT. In fact, research on muscovite as filler in PLSN has not yet been explored extensively. This is due to muscovite does not swell in water and ion exchange treatment of muscovite is not easy performed. In addition, it much cheaper than MMT. The general formula of Muscovite is $KAl_2(AlSi_3)O_{10}(OH)_2$. It is composed of monoclinic structure with a very high layer charge density, close to 1.0 equivalent per $O_{10}(OH)_2$.

2.2.4 Structure and characteristic of layered silicates

Layered silicate minerals are made of two types of structural units (octahedral and tetrahedral sheets). The tetrahedral sheets consist of individual tetrahedrons which share three out of four oxygens. They arranged in a hexagonal pattern with the basal oxygens linked and the apical oxygens (the unpaired oxygen in a tetrahedral sheet) pointing up/down. The resultant sheet composition is T_2 O_5 where T is the common tetrahedral cations of Si, Al and sometimes Fe^{3+}. The basic unit of tetrahedral sheet is a silicon atom, surrounded by four oxygen atoms forming a tetrahedron, as shown in Figure 2.3. The tetrahedra are then linked in two dimensions to form a sheet of hexagonal rings. There is also an octahedron of aluminium surrounded by oxygen atoms, and the octahedra link to form a more closely packed two dimensional sheet. While, Octahedral sheets consist of individual octahedrons that share edges composed of oxygen and hydroxyl anion groups with Al, Mg, Fe^{3+} and Fe^{2+} typically serving as the coordinating cation. These octahedrons too, are arranged in a hexagonal pattern.

The non-swelling family consist of alumina octahedra sitting on top of a sheet of tetrahedral silica, forming a dioctahedral (hence the name 1:1 family). It consists of very thin layers that are bound together with counter-ions. The basic building blocks of layered silicate are tetrahedral sheets in which silicon is surrounded by four oxygen atoms, and octahedral sheets in which a metal like aluminum is surrounded by eight oxygen atoms. Therefore, in 1:1 layered structures a tetrahedral sheet is fused with an octahedral sheet, whereby the oxygen atoms are shared (Miranda-Trevino and Coles, 2003)**.** The apical oxygen atoms from silica are shared with the aluminium atoms of the upper layer. While, the swelling clay family composes of two sheets of silica to one of

alumina (parent compound is the pyrophyllite) or two sheets of silica to one of magnesium oxide (hence the name 2:1 family). See Figure 2.4.

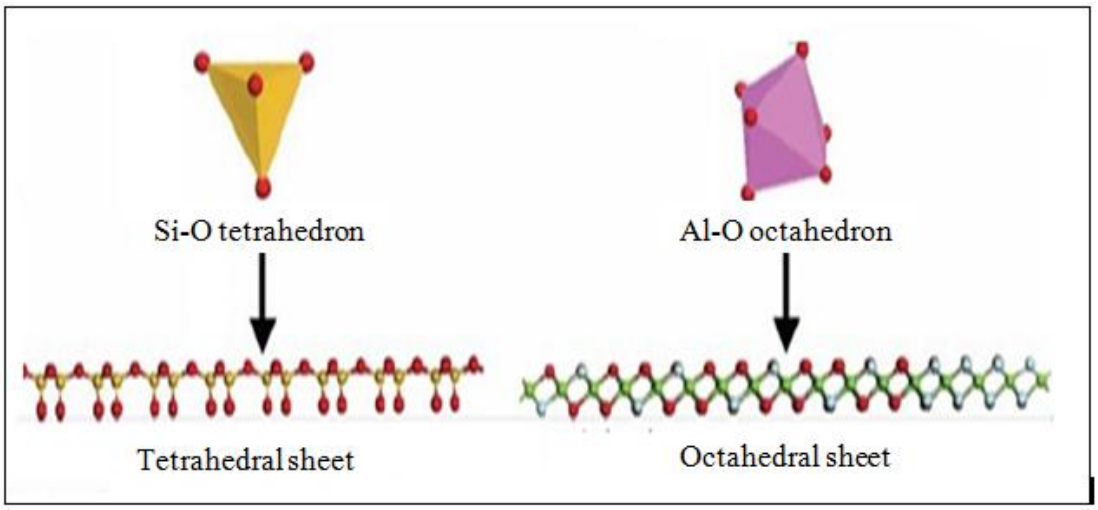

Figure 2.3: Basic structural units of layered silicate minerals(Samakande, 2008).

Generally, layered silicates that are used in the preparation of PLSNs belong to the 2:1 family. In this 2:1 family, saponite and montmorillonite have been most investigated as host materials in the intercalation because of their swelling behavior and ion exchange properties (Ogawa and Kuroda, 1997). A regular gap between the layered silicate layers due to the stacking of the layers are called the interlayer distance. Naturally, occurrence of isomorphic substitution within the layers (example Al^{3+} replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} replaced by Li^{+}) generates negative charges that are counterbalanced by hydrated alkali and alkaline earth cations situated inside the clay galleries. The resulting negative charges are counterbalanced by cations (e.g. Na^{+}, K^{+} or Ca^{2+}) residing in the interlayer spaces. The forces that hold the stacks together are relatively weak, resulting in easy intercalation of small hydrophilic molecules between

the layers. At this point the layered silicate is only miscible with hydrophilic species, e.g. water-soluble polymers such as polyethylene oxide. In order to improve miscibility with hydrophobic species it is necessary to convert the hydrophilic silicate surfaces to organophilic surfaces. Modification of the clay surfaces also increases the distance between adjacent layered silicate platelets and thus more room for larger foreign species to penetrate (Fischer, 2003b).

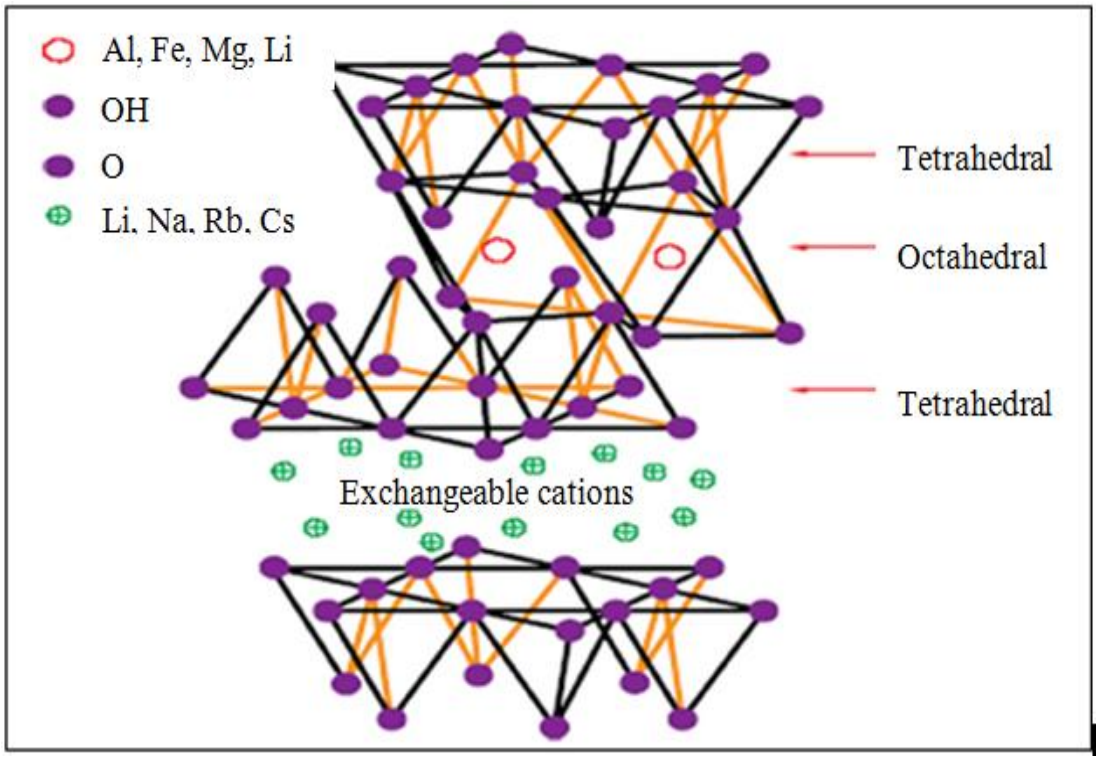

Figure 2.4 Structure of 2:1 layered silicate (Pavlidou and Papaspyrides, 2008)

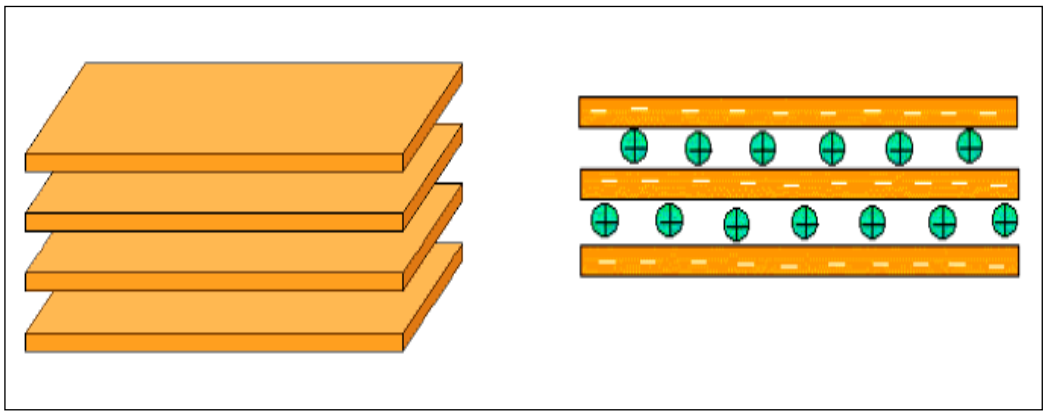

Figure 2.5 Sheet-like structures of clays

Furthermore, the commonly used layered silicates for the synthesis of PLSN belongs to the same general family of 2:1 layered or phyllosilicates. Their crystal lattice of 2:1 layered silicates, consists of two-dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedra by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets, as shown before in Figure 2.4. Depending on the particulate silicate, source of the clay and the preparation method, the thickness of the layer is around 1nm and the lateral dimensions may vary from 300A° to several microns. Therefore, the aspect ratio of these layers (ratio length/thickness) is particularly high, with values greater than 1000 (Beyer, 2002; Mcnally et al., 2003; Solomon et al., 2001).

This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC), and generally expressed as mequiv/100 gm. This charge is not locally constant, but varies from layer to layer, and must be considered as an average value over the whole crystal (Sinha Ray and Okamoto, 2003). Layered silicates have two types of structure: tetrahedrally substituted and octahedrally

substituted. In the case of tetrahedrally substituted layered silicates, the negative charge is located on the surface of silicate layers and, hence, the polymer matrices can interact more readily with the tetrahedral substituted material than with octahedrally substituted material. Generally, layered silicate minerals are divided into three major groups:

a) kaolinite group

b) semectite group

c) illite or the mica-clay group.

Among the three major groups, smectite types or more precisely montmorillonite, saponite and hectorite are the most commonly used layered silicates in the filed of polymer nanocomposite technology. Again, among montmorillonite, saponite, hectorite and montmorillonite (MMT) is the most commonly used layered silicate for the fabrication of PLSN, because it is highly abundant and inexpensive.

There are two particular characteristics of layered silicates that are generally considered for PLSN. The first is the ability of the silicate particles to disperse into individual layers. The second characteristic is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics are, of course, interrelated since the degree of dispersion of layered silicate in a particular polymer matrix depends on the interlayer cation. As a result nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers.

In general, it is well established that structural perfection is getting more and more nearly reached as the reinforcing elements become smaller and that the ultimate

properties of reinforcing composite elements may be expected if their dimensions reach atomic or molecular levels. For example, carbon nanotubes display the so far highest known values of elastic modulus. Similarly, individual clay sheets, being only 1nm thick, display a perfect crystalline structure. However, the smaller the reinforcing elements are, the larger is their internal surface and hence there is a high tendency to agglomerate rather than to disperse homogeneously in a matrix (Fischer, 2003b). In fact, the silicate layers have the tendency to organize themselves to form stacks with a regular van der Waals gap between them, which is called an "interlayer" or "gallery" (Beyer, 2002; Mcnally et al., 2003). The interlayer dimension is determined by the crystal structure of the silicate (for dehydrated Na–montmorillonite this dimension is approximately 1 nm) (Solomon et al., 2001). Analysis of layered silicates have shown that there are several levels of organization within the clay minerals. The smallest particles, primary particles, are in the order of 10 nm and are composed of stacks of parallel lamellae. Micro-aggregates are formed by lateral joining of several primary particles, and aggregates are composed of several primary particles and micro-aggregates (Ishida et al., 2000).

Basically, layered silicates cannot be a filler to form PLSN through a physical mixture of a polymer and layered silicate. Similar to polymer blends, this physical mixture leads to the formation of discrete phase. In creating PLSN, an immescible system needs to be avoided, which corresponds to conventionally filled polymers. This system favours poor physical interaction between the organic and inorganic components and results in poor mechanical and thermal properties. So, good interaction between the organic and inorganic phases is needed, where these phases are being dispersed at the nanometer level. In order to create this interaction and make it into a miscible system,

organic modification needs to be done by exchanging the alkali counter-ions with a cationic-organic surfactant, as shown in Figure 2.6**.** Where, the inorganic, relatively small (sodium) ions are exchanged with larger organic onium cations. This modification reaction has two consequences: firstly, the gap between the single sheets is widened, enabling polymer chains to move in between them and secondly, the surface properties of each single sheet changed from being hydrophilic silicate surface to an organophilic one, making the intercalation of many polymers possible. Generally, this can be done by layered silicate modification in which can be achieved by any of the four processes detailed below.

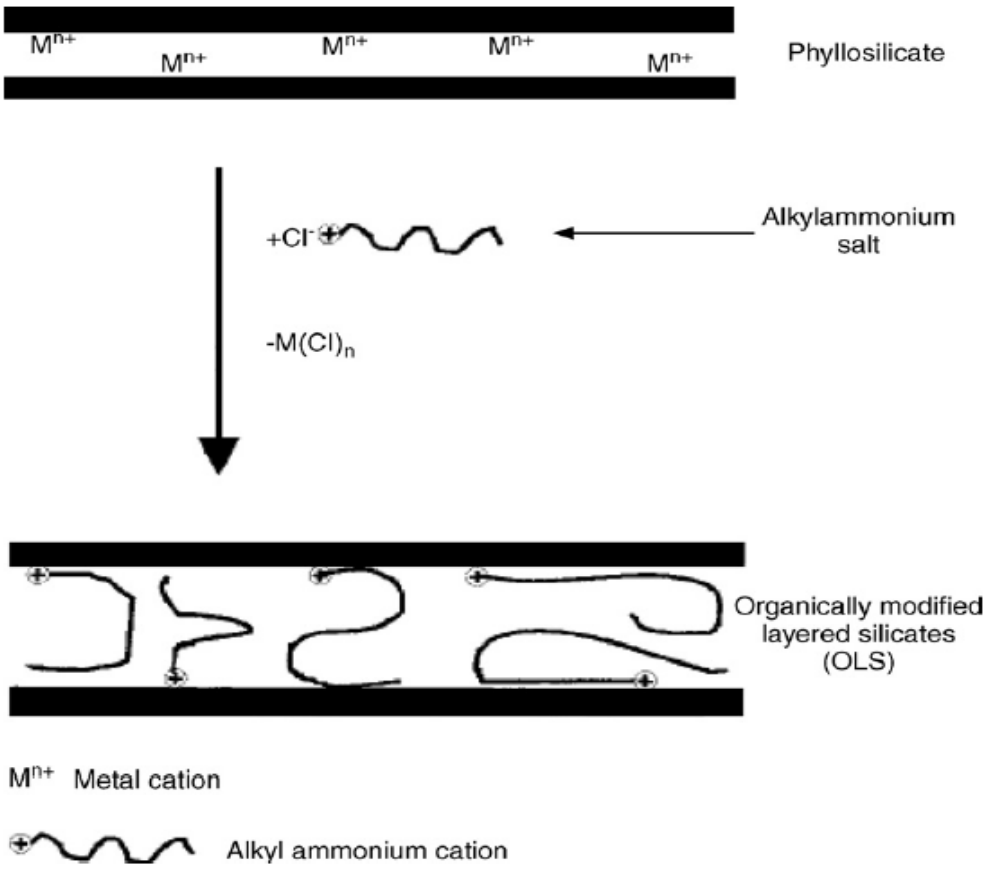

Figure 2.6**:** Schematic picture of an organic modification(Kiliaris and Papaspyrides, 2010).

2.3 Layered Silicate Modification

There are three methods of clay modification, which are:

1. Ion-exchange reactions
2. Adsorption
3. Edgewise

2.3.1 Ion-exchange reaction

Ion exchange reaction is the most common method for layered modification. It offers an opportunity to modify the surface properties of minerals by an ionically bound organic monolayer. This method is used to modify the pristine silicate by replacing small inorganic cations with any positively charged species as illustrated in Figure 2.7. The organic modification of the silicate will expand the clay galleries and matches the clay surface polarity with the polarity of polymer. In this way it is possible to promote the insertion of polymer chains inside silicate galleries.

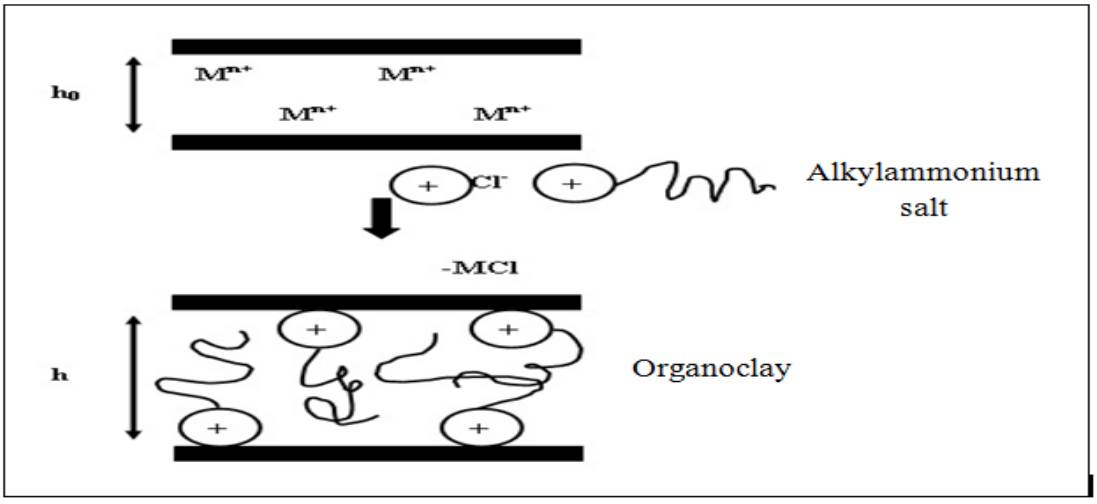

Figure 2.7: Modification of native clay by an ion-exchange on Mn^{+}, metal cation, with an organic cation.

The total number of replaceable small inorganic cations is depending on the maximum number of exchangeable sites or cation-exchange capacity (CEC). The CEC values are different depending on the types of layered silicates, which is in range of 80–120 meq/100 g of clay (Alexandre and Dubois, 2000). During the process, small hydrated inorganic cations in the layered silicates gallery spaces are usually ion-exchanged by organic cationic surfactants, such as primary, secondary, tertiary and quaternary alkyl ammonium. As a result, surface energy and cohesive energy were reduced by the organic cations and expanding interlayer distance and assisting wetting and intercalation of monomer or polymer onto the clay surfaces and into the galleries.

pH can affect the ion exchange reaction. The broken bond on the edge can also take part in the ion exchange reaction depending on the pH (Lagaly, 1999). More surfactant bind onto the layered silicates than the CEC. The orientation of the surfactant in the galleries was depending on the surfactant's chemical structure, reaction temperature, surfactant's number of tails and branching the charge density of the layered silicates. By increasing the layered silicates charge density or surfactant's chain length, it will result in larger *d* spacing and interlayer volume.

2.3.2 Adsorption

Adsorption is the process of small molecules, which can undergo dipole-dipole, ion dipole interaction or hydrogen bonding that interacts with the hydrated cation in the gallery space (Beall and Goss, 2004; Takahashi et al., 2007; Greesh et al., 2008). Greesh et al (2008) reported on the adsorption of various modifiers on montmorillonite clay using neutral and negatively charged molecules. However, it is difficult to predict the

amount of material adsorbed onto the clay surfaces when using this method. A schematic diagram of adsorption reaction is shown in Figure 2.8.

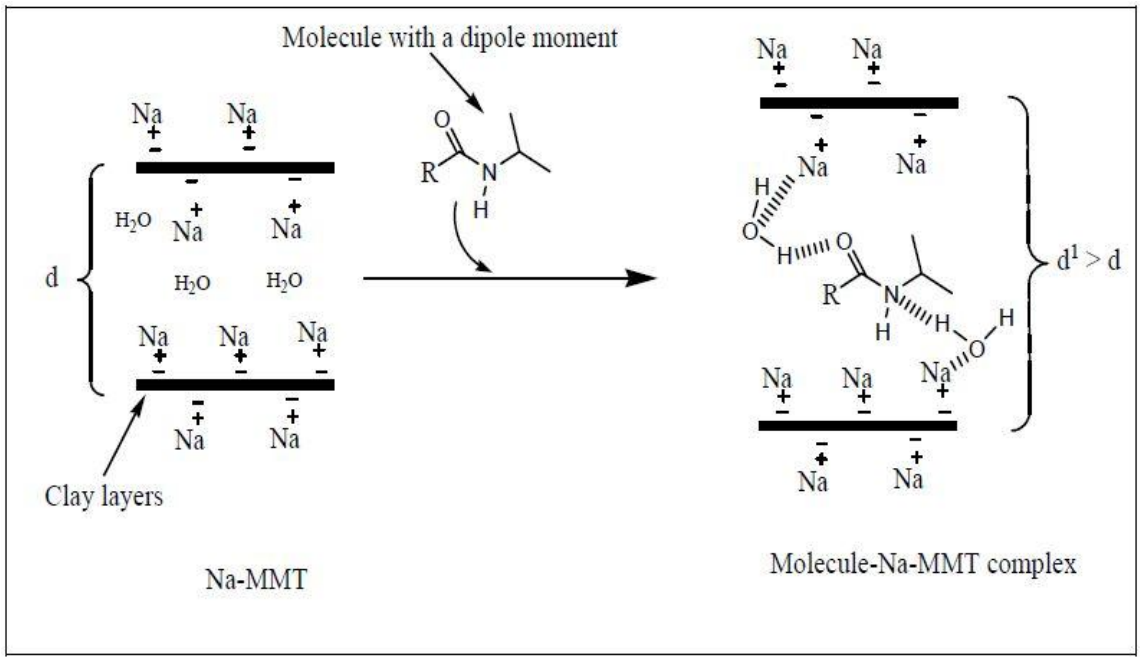

Figure 2.8: Complexation of the Na-MMT by a molecule capable of dipole–dipole interaction (Samakande, 2008).

2.3.3 Edgewise

Edge-wise is a process of layered silicates modification by using the hydroxyl groups on aluminium or silica on the edges of clay platelets. The hydroxyl groups will react with organic species to yield, in most cases, ether linkages. Silanes (Pavlidou and Papaspyrides, 2008; Ratna et al., 2003) and titanes are the most commonly used for the formation of the ether linkages during edge-wise modification. However, there is no